

Effects of carbonization conditions on the properties of coal-based microfiltration carbon membranes

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Abstract Carbon membranes, a novel porous inorganic membrane, have considerable potential applications in many industrial fields owing to their better stability in aggressive and adverse environments. However, the high cost of precursor materials has hampered their wide applications on commercial scale. In this study, coal, a cheap material, is used to prepare the tubular microfiltration carbon membranes. The effects of carbonization conditions on the properties of coal-based carbon membrane were investigated by the variation of the weight loss, shrinkage ratio of tube size and pore structure characteristics during carbonization. The results show that carbonization conditions greatly affect the properties of coal-based carbon membranes. The carbon membranes carbonized in the inert gases have more “open” porous structure and high gas flux compared to those carbonized in vacuum which makes the carbon membrane possess smaller pores and low gas flux. The carbonization temperature plays an important role in the determination of the pore structure and densification of carbon matrix. At the temperature below 600°C, the pore structure and carbon matrix of carbon membrane are formed with more

than 95% of the total weight loss and only 48% of the total size shrinkage ratio. The matrix of carbon membrane gets more compact with the temperature increasing from 600°C to 900°C, in which the size shrinkage ratio is up to 52% with only 5% of the total weight loss. The low heating rate should favor the preparation of the carbon membranes with small average pore size and narrow pore size distribution, and the high gas flow rate can produce the carbon membranes with large average pore size and high porosity.

Keywords Carbonization · Coal · Carbon membranes · Microfiltration · Pore structure

1 Introduction

Carbon membranes are novel porous inorganic membranes, which are usually prepared by carbonization of carbonaceous materials [1–3]. The recent development of industrial technology provides many new application fields for porous carbon membranes owing to their stability in aggressive (vapor or solvents, and non-oxidizing acids or bases) and adverse (high temperature and pressure operation) environments that are too harsh for polymeric membranes, which have been widely applied in water purification, wine clarification and wastewater treatment etc [4–7]. Unfortunately, the high cost of raw materials greatly limits their applications on commercial scale. Therefore, it is necessary to look for the cheap precursors for preparation of carbon membranes. Coal, as a cheap carbonaceous source with abundant deposit, especially in China, is a good candidate for preparation of carbon

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membranes, especially for preparation of microfiltration carbon membranes [8–10].

In the preparation of carbon membranes, it has been proven that carbonization conditions, such as atmosphere, temperature and heating rate, greatly affect the pore structure and separation performance of carbon membranes, and the pore structure of carbon membranes can be selectively controlled by adjusting those parameters. Geiszle and Koros had reported the influence of carbonization conditions such as atmosphere, purge gas flow rate and temperature on the properties of polyimide hollow fiber carbon membranes [11]. They found that the carbon membranes prepared in vacuum possess higher selectivity but lower permeability than those produced in inert gases. Reduction of purge gas flow rate caused a decrease in the gas permeability of carbon membranes. An increase in temperature caused a significant decrease in the permeability and increase in selectivity for carbon membranes. In the preparation of carbon membranes from Kapton polyimide precursor, Suda and Haraya found that the permeability became lower, whereas the permselectivity became higher with the increase of carbonization temperature. A low heating rate favored the increase of permselectivity, and the atmosphere hardly influenced the carbon membranes properties [12]. Centeno et al. also studied the effect of carbonization conditions on the properties of carbon membranes from phenolic resins. The results indicated that carbon membranes carbonized in an inert gas had better separation properties than those obtained in vacuum, which was different from the results obtained by Geiszle and Koros. The higher carbonization temperature and heating rates made the carbon membranes increase in selectivity and decrease in gas permeance [13]. Apparently, the separation properties of carbon membranes are greatly affected by the carbonization conditions, and the results do not follow the same law entirely for different precursors. Therefore, it is necessary to investigate the effects of carbonization conditions on the properties of microfiltration carbon membranes derived from coal in order to obtain the carbon membranes with better separation performance and uniform pore structure.

2 Experimental

2.1 Preparation of carbon membranes

The coal used for preparing carbon membranes was Ningxia coal from China, whose properties are listed in Table 1. The process employed for preparing coal-based carbon membranes is shown in Fig. 1. The coal, firstly, was ground into fine particles of less than 20 μm in diameter, and then mixed with binder into dough, which was extruded into a tube of 10 mm external diameter by a hydraulic extruder at 2.5–3.0 MPa. After drying at ambient atmosphere, the membranes were carbonized in vacuum or inert gas up to the temperature of 450–900°C at the rate of 0.5–7°C/min and held for 1 h. The final product was cooled to room temperature naturally. A schematic diagram of carbonization apparatus for both the vacuum and inert purge protocols is given in Fig. 2.

2.2 Characterization of carbon membranes

The pore structure characteristic of coal-based carbon membranes was measured by Bubble-pressure method with wetting liquid of isopropanol and porometry gas of nitrogen at room temperature. The average pore size and pore size distribution were calculated with the method recommended by Venkataraman [14]. The porosity was measured by the criterion method of China National Standards (GB1966–80).

3 Results and discussion

3.1 Effects of carbonization atmosphere on the properties of the coal-based carbon membranes

In general, vacuum atmosphere or an adequate purge with an inert gas is required to remove volatile gases and prevent undesired burn off and chemical damage of carbon membranes during carbonization [2]. The effects of carbonization atmosphere on the properties of coal-based carbon membranes are shown in Table 2 and Fig. 3.

It can be seen that carbonization atmosphere has some effects on weight loss, size shrinkage ratio and

Table 1 Properties of Ningxia coal

Sample	Proximate analysis (%)			Ultimate analysis (%)		
	Moisture	Ash	Volatile matter	Carbon	Hydrogen	Nitrogen
Ningxia coal	2.34	3.13	15.70	87.25	1.06	3.54

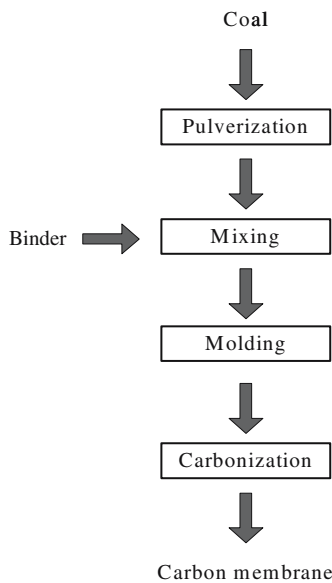


Fig. 1 Preparation process of coal-based carbon membranes

pore structure characteristic of the carbon membranes. The weight loss and length shrinkage ratio of carbon membrane produced in vacuum are higher than those in inert gases. This may be explained that the accelerated release of the volatile compounds formed in vacuum avoids the secondary condensation and aromatization reactions [15, 16]. For the pore structure characteristic of carbon membranes, the average pore size and gas flux of carbon membranes carbonized in

Fig. 2 Schematic diagram of carbonization apparatus

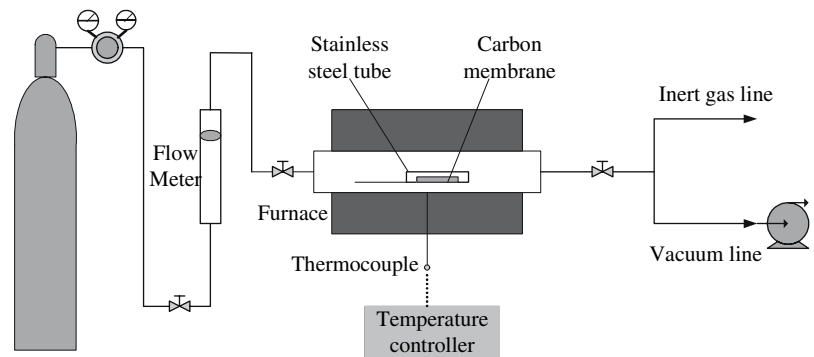


Table 2 Effect of carbonization atmosphere on the properties of coal-based carbon membranes

Carbonization atmosphere	Weight loss (%)	Shrinkage ratio (%)		Pore structure characteristic		
		Length	Diameter	Average pore size(μm)	Porosity (%)	Gas flux (m ³ /m ² s Pa × 10 ⁻⁷)
He	40.93	11.11	11.38	0.520	40.87	7.75
N ₂	41.86	11.54	12.16	0.500	40.13	7.55
Ar	41.66	11.83	12.07	0.538	40.20	7.45
Vacuum	42.30	12.57	11.21	0.448	40.42	5.32
CO ₂	44.94	12.21	12.07	0.550	41.31	7.76

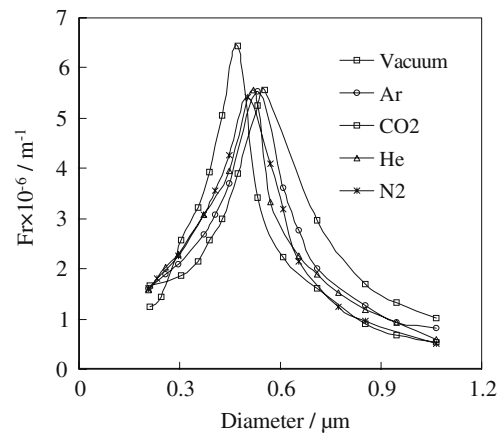


Fig. 3 Effects of carbonization atmosphere on the pore size distribution of carbon membranes

vacuum decrease obviously and pore size distribution becomes narrow, but its porosity is almost unchanged comparing with those carbonized in inert gases. It suggests that the effective pores (through hole) produced in vacuum are less than those produced in inert gases.

Little difference in properties is found among the carbon membranes prepared in He, N₂ and Ar atmosphere. However, the carbon membrane obtained from carbonization in CO₂ reveals the largest weight loss, size shrinkage ratio, average pore size and porosity due to the activation effect of CO₂ at high temperature.

3.2 Effects of carbonization temperature on the properties of the coal-based carbon membrane

Carbonization temperature is considered to be the most important parameter in the preparation of carbon membrane, because it is involved in the amount of energy required to break the chemical bonds of the raw material. The Figs. 4, 5 and Table 3 show the variations of coal-based carbon membrane properties such as pore structure characteristic, weight loss and size shrinkage ratio with carbonization temperature.

As observed, the properties of carbon membranes are strongly influenced by the carbonization temperature. The 95% weight loss of the total and only 48% size shrinkage ratio of the total occur below 600°C, and the average pore size, porosity and gas flux increase and reach the maximum at 500–600°C. With the carbonization temperature increasing from 600°C to

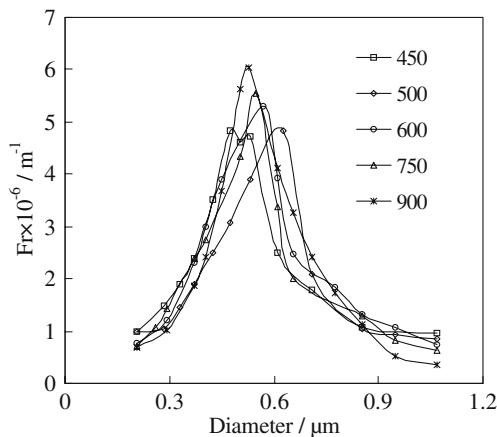


Fig. 4 Effects of carbonization temperature on the pore size distribution of carbon membranes

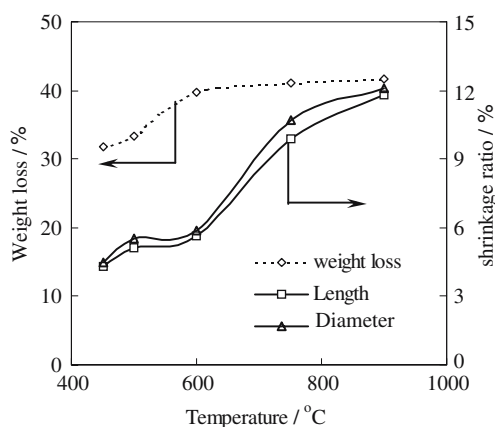


Fig. 5 The variation of weight loss and shrinkage of coal-based carbon membranes with carbonization temperature

Table 3 Effect of carbonization temperature on the properties of coal-based carbon membranes

Carbonization temperature (°C)	Pore structure characteristic		
	Average pore size (μm)	Porosity (%)	Gas flux (m ³ /m ² s Pa × 10 ⁻⁷)
450	0.500	36.04	4.48
500	0.628	39.12	6.72
600	0.560	42.97	7.56
750	0.550	42.77	7.54
900	0.538	40.20	7.45

900°C, the size shrinkage ratio is up to 52% with only 5% of the total weight loss, and the average pore size, porosity and gas flux slightly decrease and pore size distribution becomes narrow. This result suggests that there are two reactive stages during the carbonization of carbon membranes. One is the pyrolysis of coal and binder occurring below 600°C to form the carbon matrix and pore structure of carbon membranes, and the other is the arrangement of carbon structure occurring above 600°C to make the carbon matrix much more compact and the pore structure further improved [17].

3.3 Effects of heating rate of carbonization on the properties of coal-based carbon membranes

It is well known that the pore structure of carbon membranes is formed and developed by gas evolution from the matrix during carbonization. Therefore, the pore structure of carbon membrane may be affected by heating rate of carbonization, which is closely related to the rate of gas evolution and diffusion [18]. As shown in Table 4 and Fig. 6, the heating rate obviously affects the properties of coal-based carbon membranes. When the heating rate rises from 0.5°C/min to 7°C/min, the weight loss, average pore size and porosity increase, but the gas flux slightly decreases and pore size distribution becomes wide. The reason for this trend may be that a low heating rate favors the mild release of volatile compounds from the matrix and makes the carbon membranes form uniform pore structure with small pore size, whereas a high heating rate leads to gas evolution explosively and produces some irregular pore. The pinholes and microscopic cracks are also likely to be formed due to the stress resulting from the accumulation of evolved gases in carbon membranes. Therefore, a low heating rate is recommended for the preparation of coal-based carbon membranes with small average pore size and narrow pore size distribution.

Table 4 Effects of heating rate on the properties of coal-based carbon membranes

Heating rate (°C/min)	Weight loss (%)	Shrinkage ratio (%)		Pore structure characteristic		
		Length	Diameter	Average pore size (μm)	Porosity (%)	Gas flux (m ³ /m ² s Pa × 10 ⁻⁷)
0.5	41.20	11.30	12.07	0.472	40.02	7.73
3	41.66	11.83	12.07	0.538	40.20	7.45
7	43.32	11.87	12.41	0.542	40.21	7.20

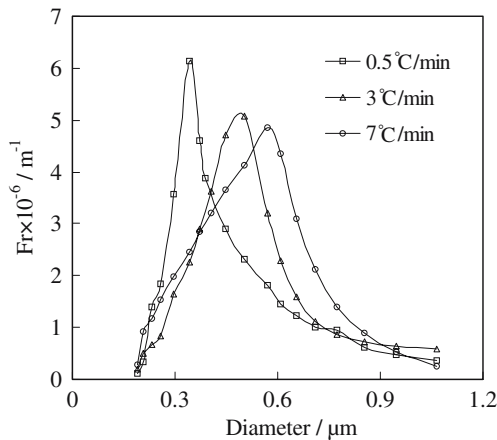


Fig. 6 Effects of heating rate on the pore size distribution of carbon membranes

3.4 The effects of purge gas flow rate on the properties of the coal-based carbon membranes

During the carbonization of carbon membranes, the typical volatile byproducts including H₂, CO, CO₂, as well as small amounts of hydrocarbons such as CH₄, C₂H₄ can be produced from matrix. An adequate purge with an inert gas is required to remove these gases. Therefore, the effects of the inert gas flow rate on the properties of the resulting carbon membranes must be considered. The results given in Table 5 and Fig. 7 show that all properties, such as weight loss, size shrinkage ratio and average pore size, increase with the augment of gas flow rate from 20 ml/min to 200 ml/min, and pore size distribution gets slightly wide. This indicates that a low gas flow rate is not sufficient to

rapidly remove the gases produced from matrix. The volatile gases such as hydrocarbon might decompose further and deposit on the surface or fill in the pores of carbon membranes. As a result, the parts of pores in carbon membranes become smaller or are blocked by carbon deposition caused by the degradation of the volatile byproducts. Therefore, a high flow rate of purge gas is needed for preparation of coal-based carbon membranes with large average pore size and high porosity.

4 Conclusion

Coal, as a cheap and abundant carbonaceous source, is a good precursor for preparation of carbon membranes. Carbonization conditions such as temperature, atmosphere, heating rate and purge gas flow have intense effects on the properties of coal-based microfiltration carbon membranes. When the temperature of carbonization is below 600°C, 95% of the total weight loss and only 48% of the total size shrinkage ratio occur. The size shrinkage ratio is up to 52% with only 5% of the total weight loss when the carbonization temperature enhances from 600°C to 900°C. The average pore size, porosity and gas flux increase and reach the maximum at 500–600°C, and the pore size distribution gets narrow at the high temperature. This suggests that two reactive stages (formation of the carbon matrix and pore structure and the arrangement of carbon structure) occur during the carbonization. The carbon membranes obtained in vacuum possess small average pore size, narrow pore size distribution and low gas flux owing to the high weight loss and

Table 5 Effects of purge gas flow rate on the properties of coal-based carbon membranes

Gas flow rate (ml/min)	Weight loss (%)	Shrinkage ratio (%)		Pore structure characteristic		
		Length	Diameter	Average pore size (μm)	Porosity (%)	Gas flux (m ³ /m ² s Pa × 10 ⁻⁷)
20	41.66	11.83	12.07	0.538	40.20	7.20
100	43.22	12.05	12.07	0.540	41.47	8.068.06
200	43.35	12.21	12.24	0.560	41.95	8.48

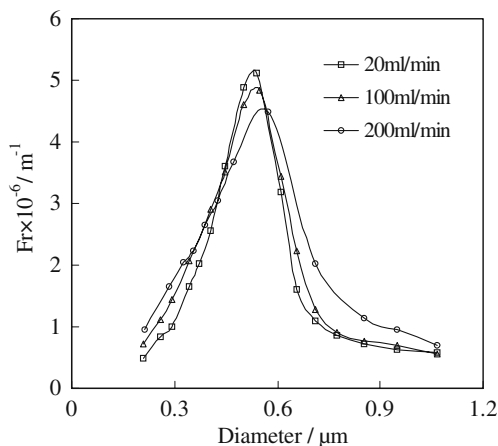


Fig. 7 Effects of purge gas flow rate on the pore size distribution of carbon membranes

length shrinkage ratio compared to those prepared in inert gases. Carbonization in CO_2 can enlarge the average pore size and porosity of the carbon membranes. The low heating rate benefits to prepare the carbon membranes with narrow pore size distribution and small pore size, and the high gas flow rate favors producing carbon membranes with high porosity and large average pore size.

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